Spin-Orbit Coupling and Ion Displacements in Multiferroic $TbMnO_3$

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The magnetic and ferroelectric (FE) properties of $TbMnO_3$ were investigated on the basis of relativistic density functional theory (DFT) calculations. We show that, due to spin-orbit coupling, the spin-spiral plane of $TbMnO_3$ can be either the *bc*- or *ab*-plane, but not the *ac*-plane. As for the mechanism of FE polarization, our work reveals that the "pure electronic" model by Katsura, Nagaosa and Balatsky is inadequate in predicting the absolute direction of FE polarization. Our work indicates that to determine the magnitude and the absolute direction of FE polarization in spin-spiral states, it is crucial to consider the displacements of the ions from their centrosymmetric positions.

Recent studies on magnetic ferroelectric (FE) materials have shown that electric polarization can be significantly modified by the application of a magnetic field [1, 2, 3, 4, 5, 6, 7]. Perovskite $TbMnO_3$ with a spin-spiral magnetic order is a prototypical multiferroic compound with a gigantic magnetoelectric effect [2]. Currently, there are two important issues concerning the FE polarization of $TbMnO_3$. One concerns the origin of FE polarization. Model Hamiltonians studies of spin-spiral multiferroic compounds have provided two different pictures. In the Katsura-Nagaosa-Balatsky (KNB) model [5], the hybridization of electronic states induced by spin-orbit coupling (SOC) leads to a FE polarization of the charge density distribution even if the ions are not displaced from their centrosymmetric positions. In contrast, the model study by Sergienko and Dagotto [7] concluded that oxygen ion displacements from their centrosymmetric positions are essential for the FE polarization in multiferroic compounds [8]. When carried out with the ions kept at their centrosymmetric positions, density functional theory (DFT) calculations [9] for the spin-spiral states of $LiCuVO_4$ predict FE polarizations that agree reasonably well in magnitude with experiment [10], which is in apparent support of the KNB model [5]. It is, therefore, important to check which model, the KNB or the "ion displacement" model, is relevant for the FE polarization in $TbMnO_3$. The other issue concerns the spin-spiral plane of $TbMnO_3$. Under a magnetic field, the spin-spiral plane of $TbMnO_3$ can be either the *bc*-plane or the *ab*-plane, but not the *ac*-plane. To explain this observation, it is necessary to probe the magnetic anisotropy of the Mn^{3+} ion. The magnetic anisotropy of the Tb^{3+} ion might be also relevant for the magnetoelectric effect, as suggested by Prokhnenko *et al.* [11].

In this Letter, we investigated these issues on the basis of DFT calculations and found that the consideration of the ion displacements is essential for the FE polarizations in the spin-spiral state of $TbMnO_3$, and the KNB model can be erroneous even for predicting the absolute direction of FE polarization. The absence of the *ac*-plane spin-spiral in $TbMnO_3$ is explained by the magnetic anisotropy of the Mn^{3+} ion.

Our calculations were based on DFT plus the on-site repulsion U method [12] within the generalized gradient approximation [13]. We used $U_{eff} = 6.0$ eV on Tb 4f states. With other U_{eff} values for Tb, similar results were obtained. For Mn 3d states, we employed $U_{eff} = 2.0$ eV, which leads to the spin exchange interactions between the Mn^{3+} ions that are consistent with the observed magnetic structure of $TbMnO_3$ (see below). For the calculation of FE polarization, the Berry phase method [14] encoded in the Vienna ab initio simulation package (VASP) was employed [15, 16], in which the Tb 4f electrons were treated as core electrons. For the study of the SOC effect associated with the Tb 4f electrons, we used the full-potential augmented plane wave plus local orbital method as implemented in the WIEN2k code [17]. Due to the small value of the spin anisotropy, we employed the convergence threshold of 10^{-7} for electron density. As shown in Fig. 1, the experimental crystal structure [18] of $TbMnO_3$ has a distorted $GdFeO_3$-type orthorhombic perovskite structure with space group Pbnm. In our calculations, the experimental structure was used unless otherwise stated.

The basic electronic structure of $TbMnO_3$ is shown in Fig. 2 in terms of the density of states (DOS) of the FM state calculated by WIEN2k with the Tb 4f states treated as valence states. The system is an insulator with energy gap of about 0.5 eV between the spin-up Mn 3d e_g states. The spin-up Tb 4f states are all occupied while the spin-down Tb 4f states occur at around -2.8 eV with the remaining down-spin Tb 4f states above the Fermi level. This feature is consistent with the f^8 configuration of the Tb^{3+} ion. Partial DOS analysis indicates that the occupied down-spin states have mainly the $f_{z(x^2-y^2)}$ orbital character with a slight contribution from the f_{xyz} orbital.

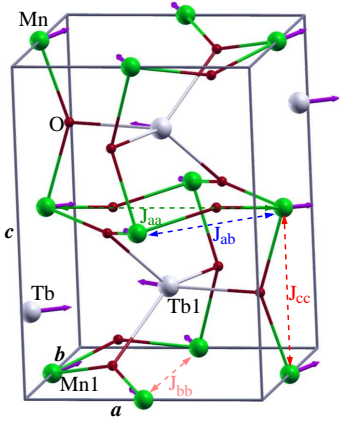For the spin exchange between Mn^{3+} ions, there are

FIG. 1: (Color online) Perspective view of the orthorhombic structure of $TbMnO_3$. The large, medium, and small spheres represent the Tb, Mn, and O ions, respectively. The Mn-Mn spin exchange paths J_{ab}, J_{aa}, J_{bb}, and J_{cc} are also indicated. The solid vectors denote the easy axes for the Tb^{3+} and Mn^{3+} spins.
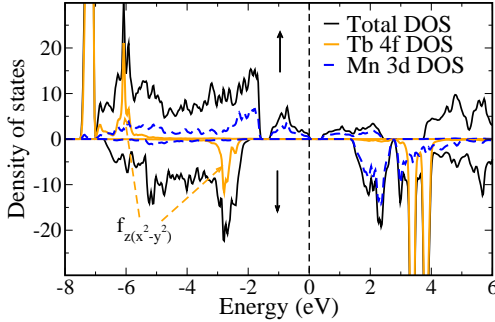

FIG. 2: (Color online) Electronic structure obtained for the FM state of $TbMnO_3$ from the WIEN2k calculations. The total DOS, the Tb 4f partial DOS, and the Mn 3d partial DOS are shown. The position of the $f_{z(x^2-y^2)}$ state is also indicated.

four spin exchange paths to consider as shown in Fig. 1: J_{ab} is the intralayer (ab plane) nearest neighbor (NN) exchange interaction, J_{aa} and J_{bb} are the intralayer next-nearest neighbor (NNN) exchange interactions along the a and b directions, respectively, and J_{cc} is the interlayer NN exchange interaction along the c direction. The high-spin Mn^{3+} ions have the $t_{2g}^3 e_g^1$ configuration with the e_g states forming a staggered orbital ordering of the $d_{3x^2-r^2}$ and $d_{3y^2-r^2}$ states. Such an orbital ordering induces an NN intralayer ferromagnetic (FM) exchange, and an NN interlayer antiferromagnetic (AFM) exchange. The co-operative Jahn-Teller distortion associated with the orbital ordering leads to a large NNN intralayer super-superexchange along the b direction [19, 20]. Our VASP calculations lead to $J_{ab} = -1.52$ meV, $J_{aa} = 0.57$ meV, $J_{bb} = 0.85$ meV, and $J_{cc} = 0.50$ meV. The calculated J_{ab}, J_{bb} and J_{cc} values are consistent with those expected for $TbMnO_3$ [19]. J_{aa} was predicted to be FM

by Kimura *et al.* [19], but our calculations show it to be AFM. The classical spin analysis based on the Freiser method [21] predicts that the spin ground state is a spin spiral with the modulation vector $\mathbf{q} = (0, q_y, 0)$ with $q_y = \mathrm{acos}(-\frac{J_{ab}}{2J_{bb}})/\pi = 0.15$. The prediction of a spin-spiral ground state is in agreement with the experimental observation [22], which shows an incommensurate spiral with $\mathbf{q} = (0, 0.27, 0)$ below 28 K. It is worthwhile to point out that if a smaller U_{eff} is used J_{bb} will be stronger, and J_{ab} be weaker, hence leading to a larger q_y.

To examine the magnetic anisotropy of the high-spin Mn^{3+} ion in $TbMnO_3$, it is necessary to consider DFT+U calculations with SOC included. $TbMnO_3$ has four Mn^{3+} ions per unit cell. The easy axes of these ions are not collinear but related by symmetry. Since the effect of SOC is largely local in nature, we consider for simplicity only one Mn ion (i.e., Mn1 in Fig. 1) per unit cell by replacing the remaining three Mn^{3+} ions with Sc^{3+} ions that have no magnetic moment. To remove any possible coupling with the Tb 4f moment, we replace the Tb^{3+} ions of the unit cell with La^{3+} ions that have no magnetic moment. The energy dependence upon the Mn spin direction obtained from DFT+U+SOC calculations is shown in Fig. 3(a) for the cases when the Mn spin lies in the ab and bc planes. The energy minimum occurs at $60°$ and $70°$ for the case when the spin lies in the ab and bc planes, respectively, and the energy minimum for the ab-plane is lower than that for bc-plane by 0.12 meV/Mn.

The above results can be readily understood by analyzing the effect of the SOC Hamiltonian [23, 24]. As shown in Fig. 3(b), each MnO_6 octahedron of $TbMnO_3$ is axially elongated. With one of the two longest Mn-O bonds taken as the local z axis and neglecting the slight difference between the other four short Mn-O bonds, the d-block levels of the Mn^{3+} (d^4) ion are described as shown on the right hand side of Fig. 3(b), which leads to the electron configuration $(xz)^1(yz)^1(xy)^1(z^2)^1(x^2-y^2)^0$. The SOC Hamiltonian $\lambda \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$ leads to an interaction of the empty $d_{x^2-y^2}$ (e_g) state with the other d-states. The strongest SOC occurs between two e_g states (d_{xy} and $d_{x^2-y^2}$) with the maximum energy lowering when the spin lies in the local z direction [24]. For the Mn1 ion, the θ and ϕ angles of the local z direction in the global coordinate system are $\theta = 80.2°$ and $\phi = 60.5°$, respectively. In good agreement with these values, our SOC analysis based on tight-binding calculations [25] shows that the actual easy axis of Mn1 has $\theta = 84°$ and $\phi = 60°$. Thus the easy axis is close to the ab plane, and is far from the c axis. This explains why the energy minimum for the Mn spin lying in the ab-plane has a lower energy than that lying in the bc-plane. In addition, the easy axis is closer to the b axis than to the a axis. Our result is consistent with the experimental observation [26] that the sine-wave modulation of the Mn magnetic moment below 40 K has the direction parallel to the b-axis. Since the easy axis of the Mn spin is far from the c direction, it is
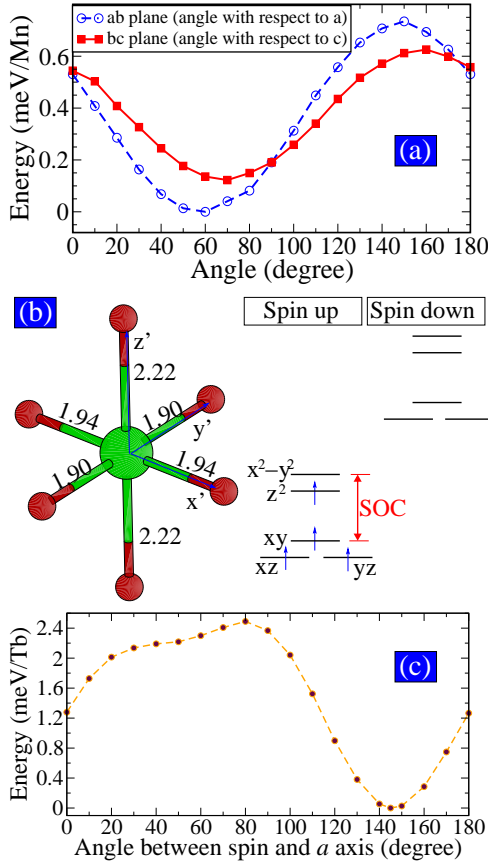
FIG. 3: (Color online) (a) The dependence of energy on the direction of the Mn spin in the ab-plane or the bc-plane. (b) The local structure of the distorted MnO_6 octahedron. The numbers give the Mn-O bond lengths in Å. The local coordinate system is also indicated. The right-hand-side diagram illustrates the electron configuration of the Mn^{3+} (d^4) ion. The label "SOC" denotes that the largest SOC mixing occurs between the d_{xy} and $d_{x^2-y^2}$ states. (c) The dependence of energy on the direction of Tb spins in the ab-plane.

expected that the spin-spiral plane of $TbMnO_3$ is either the ab-plane or the bc-plane, but not the ac-plane [27]. Experimentally [22], it was found that the Mn moments of $TbMnO_3$ form a bc-plane elliptical spiral with $m_b(Mn)$ = 3.9 μ_B > $m_c(Mn)$ = 2.8 μ_B. This can be readily explained by the fact that the easy axis of the Mn spins is close to the b axis, but far from the c direction.

The magnetic anisotropy of the Tb^{3+} ion in $TbMnO_3$ was also calculated in a similar manner; three of the four Tb^{3+} ions in a unit cell were replaced by La^{3+} ions with all the Mn^{3+} ions of a unit cell replaced by Sc^{3+} ions. Our DFT+U+SOC calculations show that the Tb spin prefers to lie in the ab plane since the state for the spin parallel to the c-axis is higher than that for the spin in the ab plane by at least 0.83 meV/Tb. The energy calculated for Tb1 (as labeled in Fig. 1 as a function of the angle ϕ with $\theta = 90°$ is presented in Fig. 3(c), which reveals that the energy miminum occurs at around $\phi = 145°$.
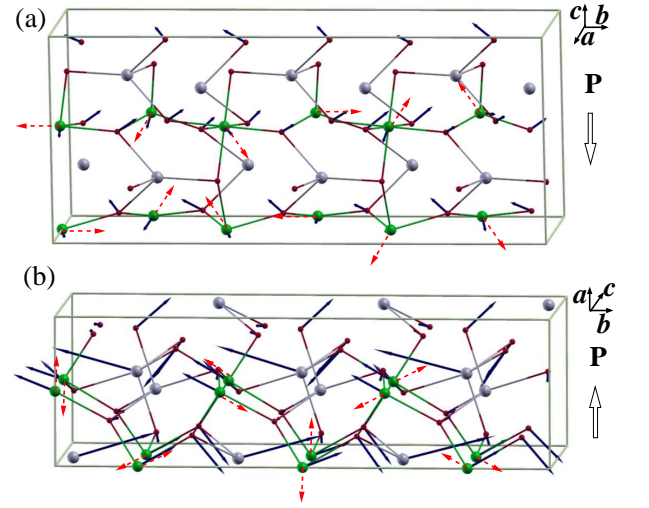

FIG. 4: (Color online) The atomic displacements (indicated by solid arrows) of the spin-spiral states after geometry optimization for (a) the bc-plane spiral and (b) the ab-plane spiral. The dashed arrows indicate the directions of the Mn spins in the spiral states. The directions of the electric polarizations are also shown.

The large anisotropy energy is consistent with the Ising behavior of Tb moment [11]. The easy axes of the Tb^{3+} ions presented in Fig. 1 show that they lie symmetrically around the b-axis with the angle 55°. This is in excellent agreement with the observed angle of 57° [26].

The electric polarization of $TbMnO_3$ in the spin-spiral state was calculated using the VASP. To reduce the computational task, we considered the $\mathbf{q} = (0, 1/3, 0)$ state, which we simulated by using a $1 \times 3 \times 1$ supercell. Using the experimental centrosymmetric structure, the electric polarization from the pure electronic effect was calculated to be $\mathbf{P} = (0, 0, 0.5)$ $\mu C/m^2$ [28, 29, 30] for the bc-plane spiral shown in Fig. 4(a). Experimentally, the magnitude of the electric polarization for the bc-plane spiral is about 600 $\mu C/m^2$ [31], which is three orders of magnitude larger than the value calculated with no geometry relaxation. For the ab-plane spiral shown in Fig. 4(b), the electric polarization is calculated to be $\mathbf{P} = (-331.0, 0, 0)$ $\mu C/m^2$ in the absence of geometry relaxation. The absolute directions of the FE polarizations obtained for the bc- and ab-plane spin-spiral states from DFT calculations without geometry relaxation are opposite to those predicted by the KNB model (Eq. 6 of ref. [5]). To examine the effect of ion displacements in the spin-spiral states on the FE polarization, we optimized the atom positions of $TbMnO_3$ in the bc- and ab-plane spiral states by performing DFT+U+SOC calculations and calculated the electric polarizations of $TbMnO_3$ using the relaxed structures. These calculations lead to P_c = -424.0 $\mu C/m^2$ for the bc-plane spiral, and to P_a = 131.2 $\mu C/m^2$ for the ab-plane spiral. The absolute directions of the FE polarizations are switched for both

spin-spiral states under geometry relaxation. The calculated FE polarization for the bc-plane spiral using the relaxed structure is now much closer to the experimental value. Furthermore, the direction of the FE polarization is in agreement with experiment [28, 29, 30, 32] as well as the KNB model. However, this agreement between the KNB model and experimental values is fortuitous; for $LiCuVO_4$ and $LiCu_2O_2$, which consists of CuO_2 ribbon chains, the KNB model predicts the wrong absolute direction of the FE polarization for the ab-plane spiral, but the correct absolute direction of the FE polarization for the bc-plane spiral, regardless of whether the unrelaxed or the relaxed crystal structures are employed [9]. The failure of the KNB model could be due to the fact that it was derived for the t_{2g} systems while the e_g states are important in Mn^{3+} and Cu^{2+} systems. Furthermore, we notice that the FE polarization of the ab-plane spiral calculated by using the relaxed structure, now along the a direction, is smaller in magnitude than that calculated by using the experimental structure. In the case of $LiCuVO_4$ and $LiCu_2O_2$, the geometry relaxation in the spin-spiral states was found to enhance the magnitudes of the FE polarizations without changing their absolute directions [9].

To show how the ion displacements break the centrosymmetry, we present the pattern of the atom displacements with respect to the centrosymmetric structure in Fig. 4. For the bc-plane spiral, the O atoms at the Wyckoff 4c position (i.e., O1) lying in the ab plane of the Tb atoms almost do not move. The movement of all the O atoms at the Wyckoff 8d position (i.e., O2) close to the ab plane of the Mn atoms have a component along the c direction. All the Mn and Tb atoms have a displacement along the $-c$ direction. The largest displacements along the c direction (about 2.4×10^{-4} Å) occur at the Mn sites rather than at the O sites. This finding is in contradiction to the assumption introduced in the "ion-displacement" model [7]. Considering that the Born effective charge is positive for the Tb^{3+} and Mn^{3+} cations, and negative for the O^{2-} anion, the total electric polarization is expected to be along the $-c$ direction, in agreement with the DFT calculation. For the ab-plane spiral, some O atoms have displacements along the $-a$ direction, but other O atoms have displacements along the a direction. The sum of the O ion displacements is along the $-a$ direction. The occurrence of alternating O displacements is consistent with the prediction made by Sergienko and Dagotto [7], and is responsible for the smaller electric polarization when compared with the case of the bc-plane spiral. All the Mn atoms have a displacement along the a direction. Another unexpected finding is that some Tb atoms have the largest displacements with a large component along the b or $-b$ direction and a small component along the a direction.

In summary, the absence of the ac-plane spin-spiral in $TbMnO_3$ is explained by the magnetic anisotropy of the Mn^{3+} ion. The calculated easy axis for Tb is in excellent agreement with the experimental result. The consideration of the ion displacements in the spin-spiral states of $TbMnO_3$ is essential in determining the magnitude and the absolute direction of the FE polarizations, which is in support of the "ion-displacement" model. Surprisingly, the displacements of the Mn^{3+} and Tb^{3+} ions are generally greater than those of the O^{2-} ions. The KNB model, however, can fail to describe both the magnitude and the absolute direction of FE polarization.

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